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## Effect of hexagonal WO<sub>3</sub> morphology on NH<sub>3</sub> sensing

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### Abstract

Tungsten oxide nano-powders were prepared by acidic precipitation from sodium tungstate solution. The alternative processes of the applied hydrothermal method resulted in different structure and morphology of hexagonal WO<sub>3</sub> nano-crystals. Micro-hotplates with gold electrodes on top to measure sensing layer conductivity were fabricated. WO<sub>3</sub> layers of the two morphologies were deposited using capillary dropping technique. Sensor responses were measured up to 220 °C operation temperature for NH<sub>3</sub> diluted in synthetic air in the 10-100 ppm range. Test results are compared in terms of conductivity, sensitivity and response time.

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**Keywords:** hexagonal WO<sub>3</sub>, gas sensor, micro-hotplate;

### 1. Introduction

Monitoring of dangerous gases in civil and industrial environment is crucial for safety, health and environmental applications. A large part of sensors must be operated in portable devices in order to provide flexibility and personal safety. Although MEMS based conductivity type gas sensors are ideal for these systems, there is still a huge effort ahead to elaborate appropriate sensors in terms of sensitivity, cross-sensitivity, response time and stability. As nano-structured metal-oxide layers in principle offer high sensitivity, the research activity was focused on the related processes and their characterization in the last decade [1]. In this work we investigate the morphology effect of nano-sized hexagonal [2, 3] WO<sub>3</sub> on gas sensing properties.

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## 2. Experimental

### 2.1. $WO_3$ powder prepared with sodium tungstate and oxalic acid - Sample A

$WO_3$  sol was prepared by dissolving 4,075 g sodium tungstate ( $Na_2WO_4$ ) in 100 ml distilled water [2]. Then, the solution acidified to set the pH 1.2 by HCl solution (3 mol/l). The precipitate was generated by added oxalic acid ( $H_2C_2O_4$ ) into the mixture and was stirred for 30 minutes at room temperature. A 50 ml volume of the obtained  $WO_3$  sol was transferred to autoclave, and then  $Na_2SO_4$  (3.33 g) was added to the solution, sealed and maintained at 180 °C for 24 h. Then the precipitates were filtered, carefully washed with water and ethanol to remove ions possibly remained in the final products. The material was finally dried at 60 °C.

### 2.2. $WO_3$ thin film prepared with sodium tungstate by Zocher method – Sample B

$WO_3$  powder was made by dissolving 4.69 g sodium tungstate ( $Na_2WO_4$ ) in 62.14 ml distilled water and the solution was kept at 4 °C for 2 h [3]. Then 33.6 ml pre-cooled HCl (1 mol/l) was added to the solution. Before washing the gel, an overnight cooling of the precipitate was applied. The resulted gels were washed with distilled water and centrifuged 5 times. Suspensions of the gels were exposed to hydrothermal dehydrations in the autoclave at autogenous pressure at 125 °C for 24 h. The obtained  $WO_3 \cdot 1/3 H_2O$  suspension was dried in exicator and the anhydrous powder was annealed at 330 °C applying a ramp up profile of 5 °C/min. The samples were maintained at peak temperature for 1.5 h in order to form the targeted  $WO_3$ .

The two types of  $WO_3$  powders prepared were dissolved in ethylene-glycol-water-ethanol solution. For deposition of gas sensing layers suspension drops were gently attached to the micro-hotplate and annealed at 200 °C for 10 minutes to remove the solvent.

## 3. Results

Morphology of *Sample A* and *B* was investigated by scanning electron microscope (Fig. 1) and characteristic geometry data of the nano-particles were also measured (Table 1).

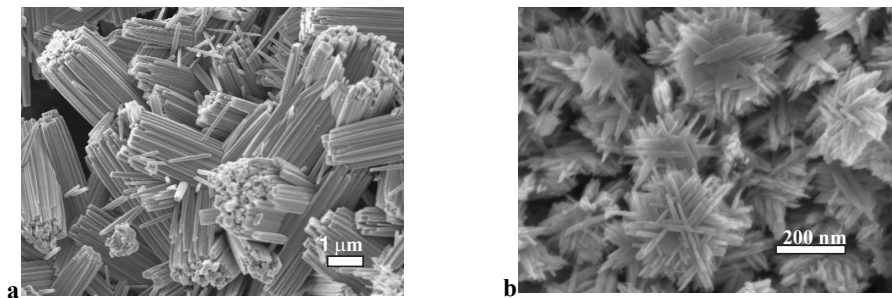


Fig. 1. (a) Sample A –prepared with oxalic acid; (b) Sample B – prepared by Zocher method. SEM views.

Table 1. Characteristic morphology data of the differently prepared samples

Sample	Oxalic acid	Additive	Morphology	Length (nm)	Diameter (nm)
Sample A	+	$Na_2SO_4$	nano-rods	400	150
Sample B	-	-	carnation	500	80

The SEM images reveal two significantly different morphologies. Application of oxalic acid and  $\text{Na}_2\text{SO}_4$  in the preparation process led to nano-rod bundles (Fig. 1. a), and in case of the Zocher method a carnation-like structured (Fig. 1. b)  $\text{WO}_3$  powder were formed, respectively.

Functional tests were carried out by depositing hexagonal  $\text{WO}_3$  on MEMS based conductivity type sensor structures. Our device is a sandwich structured non-perforated membrane with embedded Pt heater and gold interdigital electrodes on top. The membrane was released by deep reactive ion etching of Si underneath. The Pt filament and the Au interdigital electrodes were positioned in the middle of the membrane (Fig. 2.).

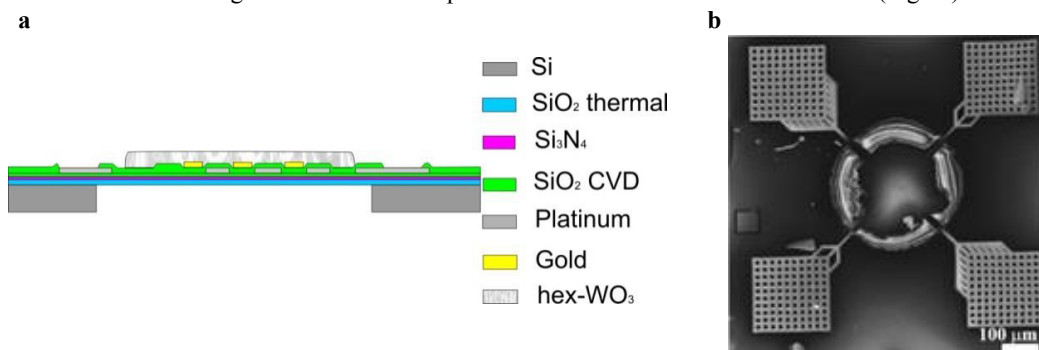


Fig. 2.(a) Schematic cross-section of the Taguchi sensor; (b) SEM image of the sensor with hexagonal  $\text{WO}_3$  nano-powder (top view).

Sensors have been tested for  $\text{NH}_3$  up to 100 ppm in synthetic air at 180 °C. The lowest detection limit is around 30 ppm in both cases, but there are a significant difference in sensitivity and response time: the carnation-like structured type B shows much better characteristics than the more compact bundles of type A.

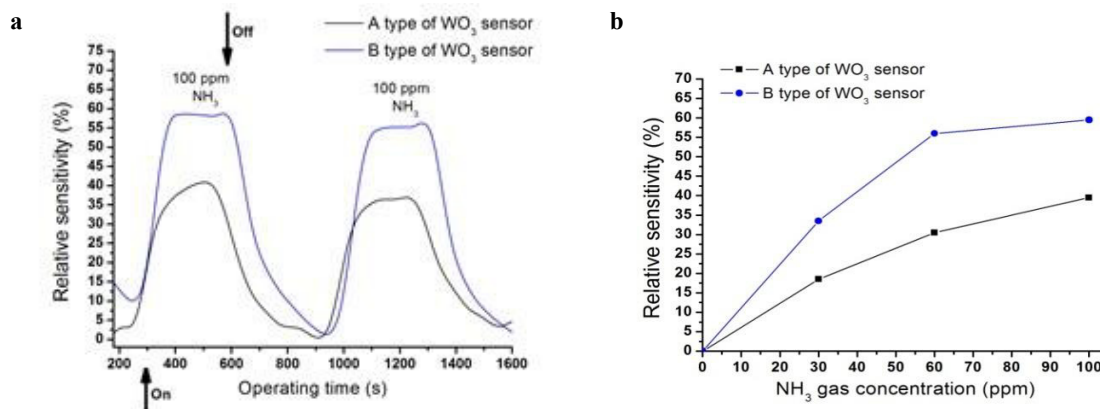


Fig. 3. (a) Response time difference between the two types of sensor in  $\text{NH}_3$ ; type A 300s and type B 50s.; (b) Relative sensitivity of the two types of  $\text{WO}_3$  sensors as a function of gas concentration at 180°C operating temperature.

In order to improve device performance the robust nano-rod boundles of  $\text{WO}_3$  powder were exposed to ultrasonic agitation to separate the nano-rods and sensors were formed to investigate the effect. Gas sensing measurements were repeated in 100 ppm  $\text{NH}_3$ . The results clearly confirmed our expectations by the presented improvements both in sensitivity and response time (Fig. 4.).

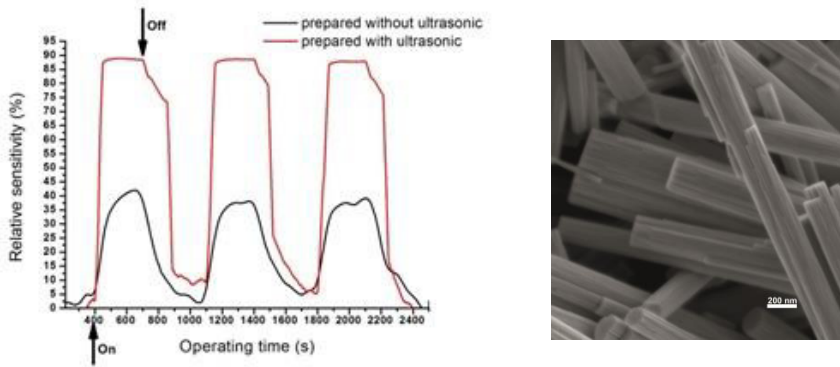


Fig. 4. Sensitivity of  $\text{WO}_3$  nano-powder prepared with sodium tungstate and oxalic acid (Sample A) with and without ultrasonic manipulation (left); SEM image of the separated nano-rods (right).

Sensitivity of ultrasonically treated *Sample A* and non-modified *Sample B* was measured at 180 and 220 °C in the range of 10 – 100 ppm of  $\text{NH}_3$  (Fig. 5.). The most effective working temperature was different; in case of carnation like structure we found it at 180 °C, while the rod type structure showed higher sensitivity and much better performance at 200 °C. Note, that the latter system is capable to detect  $\text{NH}_3$  up to 30 ppm and its response saturates at higher concentrations.

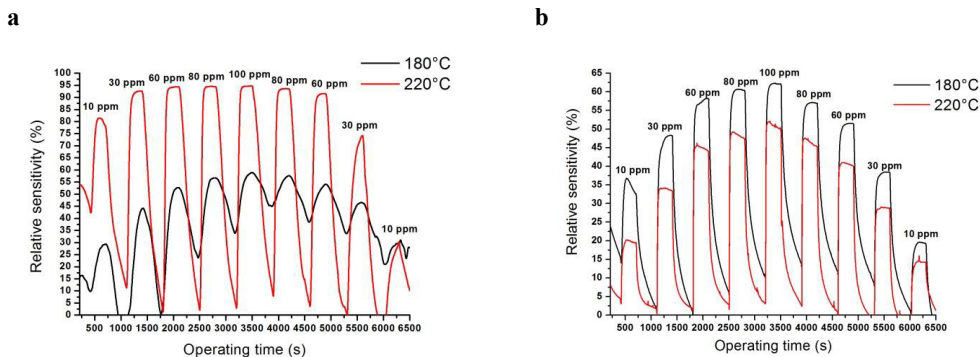


Fig 5. Sensor responses of  $\text{WO}_3$  operated at different temperatures. (a) ultrasonically agitated A type (b), carnation-like B-type

#### 4. Conclusion

Tungsten oxide nano-powders were prepared with different methods. All the alternative processes resulted in hexagonal  $\text{WO}_3$  nano-crystals but different morphologies and characteristic sizes.  $\text{NH}_3$  sensitivity measurements revealed the significance of morphology and crystallite size in device performance. Ongoing investigations of alternative processing routes may open the way towards fine tuning of sensor characteristics.

#### Acknowledgements

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